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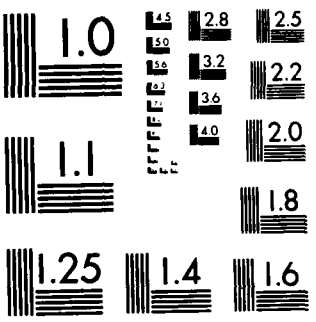

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Advanced charge transfer device (CTD) solid state array detectors offer a variety of powerful capabilities for improving spectrochemical analysis. The class of CTD detectors is divided into charge-coupled devices (CCDs) and charge-injection devices (CIDs), with each subclass having different readout modes and capabilities. While both subclasses of CTD detectors, when properly operated, provide high quantum efficiency, ultra-low dark current, low readout noise, wide dynamic range and photon integration, CIDs and CCDs possess differing capabilities suited to specific spectroscopic applications. Performance characteristics of several selected devices are presented and contrasted with those of photomultiplier tubes, photodiode arrays and several other imaging detectors. The operating parameters of CTDs including read noise, fixed pattern "noise," binning, and integration are explained and evaluated for a variety of spectroscopic applications.

Techniques for expanding a detector's operational dynamic range are discussed including random access integration (RAI), allowing optimization of the integration time for each

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different detector element based on the actual photon flux falling on each element during a specific measurement; binning, allowing the combination of charge stored in multiple elements while on the detector; and frame transfer, allowing computer summation of multiple exposures of a single analysis[1]. Keywords → to field 18

Readout modes such as random access integration are made possible in the CID because of its unique ability to readout the photogenerated charge either destructively or nondestructively. The nondestructive readout (NDRO) allows the system to interrogate each detector element to determine the level of photogenerated signal during the course of each analysis. Before detector elements associated with bright spectral lines are overexposed, they are read and both the observed signal and the integration time are recorded. Detector elements found to be monitoring weak lines are allowed to integrate until sufficient charge has been collected. On extremely weak lines, NDROs are used to reduce the system read noise and further improve the signal-to-noise ratio. No prior knowledge is needed regarding line intensity; the system determines this during the course of the analysis! Background is also measured on both sides of each spectral line for the same integration period that the line is measured, allowing sophisticated background correction to be used as necessary. When appropriate, multiple lines are observed for each element providing improved accuracy and enhancing detection capabilities.

CID detectors are available in formats ranging from one to over four million detector elements; however, since the larger arrays are rectangular instead of linear and are composed of relatively small detector elements (≈25μ), the optimum utilization of these arrays requires some degree of imagination and careful design to implement an optical system capable of providing appropriate resolution and spectral range for atomic spectroscopy[2]. Echelle spectrometer designs employing both prism and grating cross dispersers have been considered for achieving the proper optical display. Data is presented describing the current echelle system's detection limit and dynamic range performance in both simple and highly complex matrices. Detection limits for most elements are in to 1-20 ppb range. The analysis can be performed in complex matrices with almost no loss of sensitivity; for example, detection of < 5 ppb iron in the presence of 1000 ppm gadolinium is achieved.

The wealth of spectral information available during the course of each analysis can be used to provide diagnostic information either to improve the accuracy and precision, or to alert the spectroscopist that a problem exists with a given sample. For example, since the presence and concentration of organic solvents can easily be monitored by observing a carbon emission line, samples containing anomalous solvents are easily recognized. Semi-quantitative information can be obtained through the use of line ratios with an internal standard alleviating the need to prepare and run standards. Using this technique with a lutetium internal standard, the concentrations of various elements present in the ppm to the low ppb range were determined within 10%. Future trends including the development of truly intelligent atomic emission spectrometers capable of analyzing both solids and solutions rapidly and accurately with little or no previous knowledge of the sample composition are predicted.

(1) R.B. Bilhorn, J.V. Sweedler, P.M. Epperson, M.B. Denton, Applied Spectroscopy, (1987), 41, 1114.

(2) R.B. Bilhorn, P.M. Epperson, J.V. Sweedler, M.B. Denton, Applied Spectroscopy, (1987), 41, 1125.

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Array Detectors for Plasma Spectrochemistry

by

M.B. Denton, R.B. Bilhorn, R.S. Pomeroy,
J.V. Sweedler, P.M. Epperson, and R.D. Jalkian

Prepared for Presentation at the
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San Diego, California
January 5, 1988

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ARRAY DETECTORS FOR PLASMA SPECTROCHEMISTRY

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Index Headings: Atomic emission spectroscopy, direct current plasma, charge transfer device, multichannel detectors, detection limit

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Techniques for expanding a detector's operational dynamic range are discussed including: random access integration (RAI), allowing optimization of the integration time for each different detector element based on the actual photon flux falling on each element during a specific measurement; binning, allowing the combination of charge stored in multiple elements while on the detector; and frame transfer, allowing computer summation of multiple exposures of a single analysis.[1]

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